

Literature Survey of Methods to Determine
Moisture Levels in Impure Plutonium Materials

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ABSTRACT

This report constitutes a technical literature review and critique of methods potentially applicable in determining the moisture content of impure plutonium materials. The report is organized according to the nature of the techniques.

A number of *in situ* techniques are identified which are applicable to measuring water content of impure plutonium solids, and which are rapid and involve minimal (or no) sample preparation. However, in most cases substantial calibration issues complicate actual *in situ* application. Neutron moderation appears to be an almost ideal *in situ* method, if interference from strong neutron absorbers can be addressed.

Of the techniques surveyed which involve preprocessing to separate water from the host matrix prior to water content determination, those that analyze water in the gas phase are most attractive for a number of practical reasons. The most promising gas phase analysis techniques utilize infrared spectroscopy and solid-state moisture sensors, both of which are very practical to implement in a plutonium-processing environment. Infrared methods are very mature but additional technical assessment of solid state sensors is recommended for plutonium applications.

Organic liquid extraction is more complicated to implement than thermal methods in glove boxes because organic wet chemistry is involved. In this regard, supercritical carbon dioxide extraction/infrared absorption determination offers significant advantages. However, this technique is an emergent one that needs additional validation against a widely accepted method such as Karl Fischer titration.

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1. Background

1.1 Problem Addressed

Previous studies have shown that plutonium dioxide absorbs water readily from air.[1, 2] It has also been shown that hydrogen in water or other hydrogenous material in contact with plutonium dioxide can be converted into hydrogen gas.[1, 3] While its mechanism and thermodynamics remain under active study,[4-11] this phenomenon has raised concern that sealed can systems being developed for packaging impure plutonium oxide for storage could over-pressurize and rupture if hydrogenous material is not removed before the can is sealed. To address this concern, the currently applicable DOE-DP storage standard for plutonium oxides (DOE-STD-3013-96) and the proposed update include a provision that all plutonium materials be subjected to a loss on ignition (LOI) test prior to packaging.[12]

The test requires that the mass loss be less than 0.5% after heating in air at 950-1000° C for one hour. The intent of the LOI test is to assure that insufficient water remains in the calcined material to over-pressurize a container if all the hydrogen content were converted to hydrogen gas.

The LOI test was incorporated into storage standards for several reasons. It is relatively straightforward and inexpensive to implement and is proven for pure plutonium dioxide.[13] It is a conservative method in that it tends to overestimate the amount of water present in impure plutonium oxide materials, *i.e.* it can give a false positive for water. When the present standard was written, there appeared to be no acceptable alternative that did not require extensive verification.

However, efforts to implement the LOI test for impure plutonium materials have exposed the shortcomings of using an inherently non-specific technique to test more complex materials. The test materials may have more than one volatile component, or may contain components that can gain weight by oxidation during the LOI test. Indeed, both substantial mass loss unrelated to water and some mass gain have been observed in recent LOI studies.[14]

It is important to emphasize that the fundamental concern that the LOI test attempts to address is not water per se, but the potential for long-term container pressurization (due to hydrogen or other gases) under anticipated storage conditions. Therefore, any hydrogenous material that could serve as a source of hydrogen gas due to any conceivable chemical or physical mechanism over the 50-year storage design basis is of concern. Water has been the primary focus of concern to date because it is ubiquitous and PuO₂ can easily adsorb it during handling. Total hydrogen content is a more fundamental parameter related to the potential for container pressurization. However, other investigations suggest that hydrogenous materials other than water should be completely oxidized to carbon dioxide and water during the calcining step.[13]

It is clear that LOI alone is not sufficient to produce accurate moisture content determinations for all impure plutonium materials.[14] Passing an LOI test in most instances may ensure that material is free of hydrogen-generating potential. However, a large number of false positive results may also ensue due to volatilizable salts or other innocuous constituents, resulting in additional analysis and or stabilization requirements for many samples.[15] The LOI test could be used in conjunction with other analytical techniques that can distinguish between the volatile components responsible for mass loss. Alternatively, the LOI test could be replaced completely by a more hydrogen-specific

analysis technique. Laboratory-scale evaluation of several approaches currently is underway in the DNFSB 94-1 Lead Laboratory Research and Development Program.[16, 17] This report addresses the need to place these efforts in a broader context by summarizing the published literature on a broader range of analytical techniques that might be applicable to the problem.

1.2 Report Scope

This report presents the results of a broad survey of the analytical chemistry literature aimed at identifying analytical techniques that may be applicable to quantitative detection of water in impure plutonium oxide. This report is not a comprehensive survey of all analytical techniques applied to water determination, but it is broad enough to call attention to promising techniques used in other industries. Many of the techniques mentioned may not have been considered previously for this type of application.

This literature survey does not include all moisture determination techniques found in the literature, because some are clearly not applicable to plutonium environments, some have been superseded by more modern techniques, and some are insufficiently sensitive. In cases where enough information to determine applicability of a technique was lacking, the technique at least has been mentioned. A selected subset of the literature is referenced for each technique included. A comprehensive bibliography could be produced later for the most promising techniques, if necessary.

The scope of this review also does not include a comprehensive examination of the patent literature. We have cited selected patents to illustrate the extent of the literature, but there are many more that could be just as relevant.

Some techniques are included that may not have adequate sensitivity toward water in plutonium materials (0.5 weight percent is the moisture criterion in the storage standard). We have elected to be conservative by including apparently marginal techniques, because they may have been improved substantially since the publication of the references. They also may have the potential for future improvements.

Several comprehensive reviews of analytical techniques, for determining water in a variety of solid matrices, are available.[18-20] It is beyond the scope of this report to critically evaluate the applicability of every technique mentioned in these reviews. Instead, we have grouped potentially applicable methods into general categories that share characteristics of sensitivity and applicability, and then offered some critical comments. We have included more references from the literature on instrumental techniques that appear to have advanced considerably since earlier publications. This approach should not be construed as a judgment that more recently developed techniques are more likely to prove useful. It is an attempt to place newer techniques on an equal footing with older techniques that had already been reviewed extensively.

Relevant literature was located by searching the CAPLUS online database produced by the Chemical Abstracts Service, Columbus, Ohio. This database consists of all Chemical Abstracts entries from 1968 to the present. The SciFinder™ search engine, also by Chemical Abstracts Service, was used to perform the searches.

1.3 Report Organization

Methods described in this report are divided into those that can be applied to the host matrix without processing to remove water (*in situ* methods) and those that involve removing the

water from a sample prior to or during analysis (*ex situ* methods). *In situ* does not imply that the material is necessarily examined in its storage container, but rather that the water is determined without removing it from the matrix. *Ex situ* techniques are further subdivided into those in which changes in the host matrix are analyzed during water removal, and those in which the removed water is detected directly. We also consider an additional class of methods that measure total hydrogen content rather than water content *per se* as an alternative means to bound the potential for hydrogen gas generation. The chart below (Fig.1) summarizes the relationships between these classes of methods. Members of those classes outlined in bold are explicitly discussed in this report. This organization was chosen because it groups methods by their common advantages and disadvantages relative to the requirements outlined above.

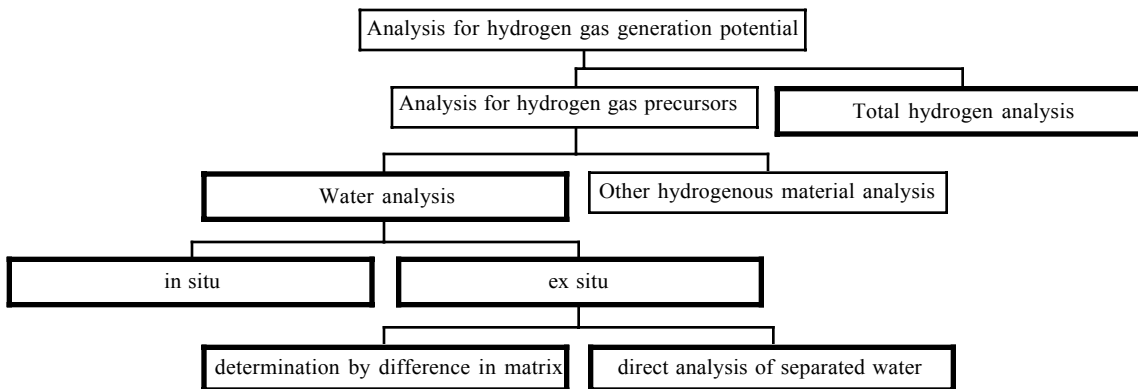


Fig.1 Classes of analysis and their relationships

Characteristics of an ideal technique for the determination of water content of impure plutonium materials include the following:

- 1) high specificity for water in the presence of most or all anticipated matrix components,
- 2) sufficient sensitivity to detect <0.5 weight percent water with high reliability, without regard to how tightly the water is physically or chemically bound in the solid matrix,
- 3) minimal uncertainties due to sampling an inhomogeneous analyte,
- 4) reliability for all expected impure materials in the absence of prior detailed compositional knowledge,
- 5) practical deployability and operational reliability for repetitive analyses in a plutonium processing environment,
- 6) acceptability of installation and operational cost,
- 7) short analytical turnaround time,
- 8) technical maturity.

As each technique is described below, we indicate our perception of how well these criteria are met. Our conclusions guided by these criteria are summarized in Table I.

2. In Situ Methods

In situ methods share the characteristic that they quantify water while leaving it undisturbed within the host. This classification does not imply determination within the storage container, although this may be possible in some cases.

In situ techniques have the potential advantages of simplicity and rapidity of analysis. These advantages must be weighed against disadvantages of possible host matrix interferences. Because the host often perturbs the measured moisture signal, calibration of *in situ* techniques in the same or a similar host matrix is usually necessary for quantitative

determination. For the latter reason, these methods are often grouped together as indirect or secondary methods.

A great deal of recent research and development on *in situ* methods of water analysis has been driven by the food and fuel industries, as can be seen in the titles listed in the bibliography. Soil science has driven significant development work in microwave and lower-frequency techniques. The resulting literature is extensive and tantalizing. However, the literature does not provide definitive answers on the suitability of these techniques for impure plutonium materials water determination. For example, the target water concentrations in food, fuel, and soil are much higher than 0.5 weight percent, usually several weight percent and often tens of weight percent. Thus, the issue of sensitivity to <0.5 percent water is difficult to assess from the existing literature for most *in situ* techniques.

2.1 Neutron Moderation

Neutron moderation techniques measure the total concentration of hydrogen atoms by bombarding the sample with fast neutrons and detecting the neutron moderation induced by the sample.[21-30] Since hydrogen atoms are very good neutron moderators and PuO_2 and most of the other impurities are not, hydrogen atoms are detected with only a few (but significant) interferences. Unlike most *in situ* techniques, sample inhomogeneity, morphology and detailed composition are not major concerns. Sensitivity appears to be easily sufficient to meet the 0.5 weight percent requirement for this application.[16] Hydrogen atoms in different chemical environments are not distinguished, so if hydrocarbons or other hydrogen containing materials are present, they will not be distinguished from water. However, this feature is an advantage for this application because it allows detection of all possible hydrogen gas precursors in the sample.

Determination of moisture in coal is the most common current application of neutron moderation in the literature we reviewed. Instrumentation is very practical to use in a plutonium-processing environment and initial instrumentation costs are moderate. A significant current limitation of neutron moderation for plutonium materials applications is interference from strong neutron absorbers such as uranium and beryllium.

Calibration tests of neutron moderation techniques for moisture analysis of impure plutonium materials are being carried out in the DNFSB 94-1 Lead Laboratory Program.[16] A final recommendation on the application of the method is expected in February 1999.[31]

2.2 Infrared Absorption

Infrared absorption (IR) methods have been used widely in food, fuel and other industries for water analysis.[32-41] IR methods detect water primarily through quantitative measurement of the intensities of OH vibrational resonances in the infrared and near-infrared regions. Because these techniques can compare absorption at different energies where water and potentially interfering constituents do not overlap, there is excellent selectivity for water. Both reflectance and transmission modes have been used, depending on the transparency of the sample. Because water is a strong absorber, this technique can be quite sensitive. Water concentrations of about 20 ppm have been detected in glasses and crystals by IR transmission.[38]

A number of difficulties complicate the application of *in situ* IR methods to impure plutonium materials. For example, the apparent IR absorbency depends upon scattering and absorption by the host matrix, as well as the perturbation of the water vibrational

spectrum by the host. Calibration usually is required using well-characterized samples as standards. These standards must have optical characteristics and chemical interactions with water very similar to those of the host matrix as standards. This requirement would be impractical for the broad range of impure plutonium materials that must be tested.

2.3 Microwave, Radio-Frequency, and Time Domain Reflectometry

These related techniques are based on mature technologies for generating, detecting and analyzing microwave and radio frequency (rf) energy. We have grouped these techniques together because they are based on measuring the same properties of water in the host matrix using the same region of the electromagnetic spectrum. The literature contains many examples of techniques in this group.[23, 26, 28, 42-82] In some cases, different names have been given to the same technique by different investigators. Moreover, where real differences do exist, they are not significant for the purposes of this evaluation. These methods share common advantages and disadvantages for the subject application.

The unifying principle of these techniques is that they all involve irradiation of samples with rf and/or microwave energy followed by measurement of attenuation and phase shift after the radiation passes through a region of the sample. The determination of water content is based on the large difference between the dielectric constant of water and the dielectric constants of the host matrix and impurities at these frequencies. The techniques can be sensitive enough for remote sensing, as evidenced by their use to determine soil moisture from airplanes and from outer space.[51, 52] Many instrumental designs are used, depending on the frequency and type of material.

Time domain reflectometry is a variant in which the dielectric response of the analyte is measured by measuring the time-resolved reflection of an electromagnetic pulse. A Fourier transform is applied if the frequency response is desired. The information extracted is essentially the same as that from a microwave spectrum measurement. Water sensitivity to a few weight percent has been demonstrated in water/oil emulsions and in biochemical systems. Much recent literature describes applications in soil science, where the attractiveness of this technique is that probes can be engineered to measure soil moisture in the field, including depth profiling.

Microwave and radio-frequency techniques share the generic disadvantages of most *in situ* techniques because the effects of variability of the host matrix must be first determined, and an independent calibration for each type of matrix made. It is difficult to judge whether sensitivity would be sufficient to detect 0.5 percent water in impure plutonium materials prior to performing microwave and rf calibrations. Most published applications target higher water concentrations, but that may be due to the industrial problems to which the technique has been applied rather than to intrinsic limitations. A few reports quote good sensitivity, such as one claiming 0.1 weight percent sensitivity to water in a plastic[54] and a detection limit less than 100 ppm in some dielectrics.[58]

A potentially severe limitation of microwave and radio frequency techniques is that strongly conducting materials (salts, metal, etc.) are powerful absorbers. The presence of such materials in or around the sample may make this family of techniques impractical for many plutonium containing materials. There are recent probe designs that are claimed to overcome conductivity problems, but it is not clear whether these address the specific problems that are presented by impure plutonium oxides.[45]

2.4 Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) has been used to measure water content in the food, fossil fuel, and building materials industries, among others.[46, 83-97] The measurement is based on the fact that protons in a magnetic field absorb rf energy due to a resonance between nuclear spin states split by the field. The energy, intensity, and time-dependent behavior of this resonance depends upon the chemical environment of the proton, enabling the technique to selectively detect protons in a particular molecular environment within a material containing other protons. Field gradients and sample translation have been used to measure water content of samples in one, two and three dimensions.[90, 92, 96, 97]

Published literature is insufficient to determine whether NMR affords sufficient sensitivity or freedom from interferences to measure water in plutonium materials. Most published literature refers to materials with water content around 10 wt. %, for example in grain and coal. However, sensitivities of 0.2-2 wt. percent were reported for some matrices a number of years ago.[90, 92] Furthermore, plutonium oxides are paramagnetic, and paramagnetic materials interfere affect NMR signals. Recent work on spatial profiling of moisture in building materials with high iron content suggests that the paramagnetic host problem may not be insurmountable.[96] But the specific problems presented by detection of proton signals in the presence of Pu need to be investigated before it is possible to determine whether this technique is viable.

In a recent preliminary report, detection of 0.6 wt. % water on uranium dioxide was demonstrated with good signal to noise (500 ppm reported sensitivity) in a toroidal cavity.[98] While the uranium results are promising, extension to plutonium and to impure materials may present significant difficulties. The authors discuss, as future work, their intention to extend these studies to PuO₂ and at least imply that the extension from U to Pu will not be difficult. There is minimal NMR literature on Pu-containing materials to support this expectation, however. Also, sample matrix variability with respect to magnetic properties could present difficulties that are not discussed. It would be prudent to await the actual Pu results before concluding whether this is a viable technique for the proposed application.

More limiting to the application to plutonium oxides is that NMR instrumentation is relatively expensive to install, and is problematic to operate and maintain in a plutonium-processing environment. Recent results suggest that less expensive low-field instruments may be usable in place of very expensive, solids-capable, high-field instruments for moisture analysis, but this is not mature technology for this application.[97] The cost and implementation difficulties are unlikely to be justified for overall water or hydrogen determination, but might be justified if a greater need arose for the unique capabilities of NMR to examine details of the chemical and spatial[98] distribution of hydrogen.

2.5 X-ray Diffraction

Water of crystallization in crystalline materials is manifested in x-ray powder diffraction patterns. Water content in such materials can be quantified accurately by X-ray diffraction analysis.[18] Water loss during heating in principle can be monitored by changes in X-ray diffraction patterns, but this generally requires prior knowledge of the powder pattern and structure of the dry material. Very few impure plutonium materials will fulfill these requirements. Furthermore, size of the sample subjected to x-ray analysis is small, so the method is poorly suited to heterogeneous materials. Another serious disadvantage is that x-ray methods will not detect water adsorbed to surfaces or covalently bound to amorphous materials. X-ray methods also are difficult to implement in routine plutonium process environments.

3. Ex Situ measurement of host matrix after water removal

Each of the detection techniques discussed in this section has been used successfully to characterize water lost from host matrices after heating. They share the characteristic of not measuring water directly but rather measuring host mass loss or changes in other bulk properties of the host upon removing water. Thus, selectivity for water requires that constituents other than water not contribute to changes in these bulk properties upon heating, or contribute in known ways that can be accounted for in the determination. Most of these techniques are more selective than purely gravimetric determination of total volatile substances, but they share many of the same disadvantages because they do not detect water directly.

3.1 Loss on Ignition

Simple gravimetric methods, often referred to as Loss on Ignition (LOI), have been used for centuries to measure the difference in sample mass difference in a specified heating cycle. LOI tests can take place in air, under an inert atmosphere, or in vacuum. LOI is a primary technique in many widely used procedures for analyzing water in solid hosts, particularly if the host is stable at high temperature. The method is straightforward to implement in most environments and results are easy to interpret for simple materials.

The primary disadvantage of LOI is that it is not specific for water if other volatile materials are present in the host matrix. Many impure oxide samples will appear to have high water content when they in fact some other volatile component is being driven off. Those samples that fail the LOI test for this reason will need to be calcined again and/or analyzed more extensively. In addition, if oxidizable constituents are present, mass gains can occur during the test and/or offset mass loss of evolved constituents. Reliable practical application of LOI to measure water content of impure plutonium oxide materials therefore is not possible without prior compositional knowledge or application of auxiliary methods. All samples of impure oxides of less than 80% Pu content tested to date have failed the standard LOI test.[13]

3.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a gravimetric approach in which the mass loss of the host matrix is measured continuously as temperature is increased in a controlled fashion. Selectivity for water is better than LOI since mass loss is quantified into a series of temperature-dependent steps, some of which may be more likely to be due to water loss based on experience with similar matrices, and some of which may be assignable to other volatile substances. Commercial instruments with large sample capacities may be available. However, since sample size is generally small for most instruments (mg to gram scale), sampling heterogeneous material can be a serious concern. Another major drawback is that, like LOI, it does not provide unambiguous information that the measured mass change is due to water loss. TGA instrumentation is mature, inexpensive, and readily adaptable to a plutonium process environment.

3.3 Differential Thermal Analysis / Differential Scanning Calorimetry

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are calorimetric techniques that measure specific heat capacity in a sample and that can do so over a wide range of temperatures. Changes in this specific heat capacity may be induced

by composition changes such as loss of adsorbed water, and by phase changes. Apparent changes in specific heat capacity can also be caused by loss of overall sample mass even if there is no change in the true specific heat capacity. DTA and DSC are often combined in a single instrument package. Like TGA, DTA and DSC provide more information than LOI because they allow one to record and analyze changes in the measured property as a function of temperature. These methods are not inherently specific for water. If these methods are calibrated using independent, water-specific analysis techniques on the range of host matrices that are expected, and if the effect of water volatilization can be shown to be separable from that of volatilization of other components, moderate specificity for water might be realized in practice. Like TGA, these methods use small samples and therefore multiple samples would be required to achieve accurate results for heterogeneous materials. In addition, like TGA, DTA/DSC instrumentation is mature, inexpensive, and readily adaptable to a plutonium process environment.

3.4 Thermal and Mass Spectrometry Combination Techniques

Hybrid instruments are now available that add a mass spectrometer (MS) to TGA/DTA/DSC to analyze gases evolved during stages of heating. This is a powerful enhancement of the gravimetric and thermal techniques described above because MS allows real-time identification of the volatile substance(s), whose loss may be contributing to the measured sample mass loss or to the measured change in specific heat capacity. Thus, MS addresses the major shortcoming of the stand-alone thermal techniques. The combination also is better than MS alone because it relies on MS for qualitative identification of volatile materials but not for their accurate quantitative determination. Small sample size remains a serious concern for characterizing heterogeneous materials. MS also can add significantly to the instrumentation cost and ease of operation in a plutonium environment.

4. Ex Situ Gas-Phase Analysis of Evolved Water

It is assumed in DOE Standard 3013-94, -96, and the current proposed update that heating to temperatures of 950-1000 °C for several hours is sufficient to volatilize essentially all water in impure plutonium materials. In principle, quantitative water measurement can be achieved by detection of water after it has been volatilized. Many techniques have been used successfully to detect water in the gas phase, which have advantages over *in situ* techniques. For example, with gas-phase methods neither matrix heterogeneity nor matrix effects on the water are of concern in the analysis stage, though heterogeneity is still of overall concern if the size of the heated solid sample is small. Gas phase measurements possess a major advantage over gravimetric and other host-based property measurements in that water can be detected specifically in the presence of other volatile substances with much greater ease.

On the other hand, gas phase techniques depend upon the ability of heating to remove all water from the host. Furthermore, because water volatilization into the flowing gas stream that is commonly used reduces the gas phase water concentration, intrinsic sensitivity must be higher than *in situ* techniques. However, low background signals in the gas phase usually is more than adequate to compensate for dilution.

There are several complications in glove box implementation of gas phase water detection. For example, gas-handling systems must be employed and the notorious affinity of water adsorption on surfaces must be taken into account. This category of techniques requires heating of the sample, which is a disadvantage compared to *in situ* techniques. Additional implementation issues depend on the complexity of the specific water detection instrumentation, as discussed below.

4.1 Gas-Phase Infrared Spectroscopy

In gas-phase infrared methods, absorbances due to water stretching or bending vibrations are detected. An extensive literature exists on this technique, of which we include only a few key references in the bibliography.[76, 99-104] Quantitative gaseous IR water determination is more straightforward than *in situ* IR because the spectrum of water in the gas phase is more easily interpreted than in solid matrices. Thus, interferences are more easily managed. Specificity for water in the presence of other volatile substances is excellent and sensitivity should be sufficient for plutonium materials application as long as the dilution by the carrier gas is not too great. Our literature search found reported sensitivities as good as 30 ppb.[103] Compact, rugged, inexpensive IR instruments are available that are readily adaptable to plutonium glove boxes. Non-dispersive and dispersive gas-phase IR methods in an interstitial gas analysis system are currently being evaluated in the DNFSB 94-1 Lead Laboratory Program in an effort led by D. Vance.[105]

Disadvantages of gas-phase infrared methods may include small sample sizes, the need for sample heating, and the need for gas collection with the associated potential for losses due to water adsorption on walls. Instruments larger sample sizes may be available or easily built, however.

4.2 Electronic Gas-Phase Moisture Sensors

The patent literature contains many references to solid-state moisture sensors based on the effects of adsorbed water on the capacitance or resistance of insulators, or on the conductance of semiconductors.[106-115] Many patents exist for other electronic devices using different materials or interrogation techniques. We have not investigated this patent literature critically, nor have we investigated the numerous commercial products based on these techniques. However, because these technologies appear to be sensitive and easy to implement in a glove box environment, they should be evaluated further.

4.3 Mass Spectrometry

In mass spectrometry (MS), constituents in a gas mixture are identified by molecular mass and fragment masses using a mass spectrometer. Thus, MS can be highly selective and readily distinguishes water from other volatile components. Plutonium glove box implementation is feasible using rugged, relatively inexpensive quadrupole instruments. MS methods are currently being evaluated in the DNFSB 94-1 Lead Laboratory Program.[105]

In the implementation described here, MS, like all the techniques in this section, requires heating the sample to volatilize water. An additional major disadvantage of MS is that quantitative measurement can be problematic because of the strong tendency of water to adsorb to surfaces of the instrument's gas handling system. Use of a carrier gas and heated tubing mitigate this problem, but accuracy and sensitivity still are problematic.

4.4 Gas-Phase Thermal Conductivity

Moisture-laden gas has a different thermal conductivity (TC) than dry gas. Instruments are commercially available to detect this difference and quantify gaseous water concentration. They are probably relatively inexpensive and simple to operate, although we have not verified this. A disadvantage relative to other detection techniques in this section is that TC

methods are less specific for water. Other evolved gasses could produce a positive signal. Trapping of other gaseous constituents before the TC detection would eliminate this interference, but would add complexity to the measurement procedure and instrumentation. Other disadvantages are common to all techniques in this section and are discussed above.

4.5 Microwave and Radio-Frequency

The application of microwave and radio frequency techniques to measure water content of solids was described in the earlier section on *in situ* techniques. Microwave methods also have been used to quantify water in the gas phase.[71, 76] The literature for application to gases is much less extensive than for solids. It seems reasonable that interferences would not be the significant problem that they would be in solid matrices. Specificity might be greater than some other gas phase detection techniques, such as thermal conductivity, but would be less than others such as IR or MS. Implementation would probably be easier than most other techniques in this section. Disadvantages include those common to all techniques in this section, as discussed above.

4.6 Cryo-Trapping of Evolved Water and Subsequent Measurement

This is not an analytical technique in itself, but rather a potential enhancement to other techniques. Water evolved from heated solids can be collected in temperature-controlled cryogenic traps. The concentrating process can be used to amplify the sensitivity and selectivity for water over other volatile constituents using many detection techniques. For example, cryotrap systems might be operated so that other volatile substances either pass through or condense in warmer or colder regions of the system.[18] Cryosystems could be inexpensive, rugged, and easily implemented in plutonium glove boxes. Cryo-traps might be added as enhancements to many moisture determination systems including IR and LOI. To our knowledge, there has been no work on implementing this concept for this or similar problems in a plutonium environment, so development work would be required. Additional disadvantages include those common to all techniques in this section, and those associated with whatever method is used to quantify the trapped water.

4.7 Collection of Water on Absorbers

Many solid materials have a high affinity for water and can be used to collect water from a gas stream. The water content of a sample can be inferred by weight gain or other chemical or physical change in the absorber due to uptake of water evolved from the sample. An example of this type of technique in this category is the use of a film of $\text{H}_4\text{P}_2\text{O}_7$ to determine water content in PuO_2 . The $\text{H}_4\text{P}_2\text{O}_7$ film reacts with water evolved from heated PuO_2 to form H_3PO_4 , which in turn is oxidized electrochemically to regenerate $\text{H}_4\text{P}_2\text{O}_7$. Water is then quantified coulometrically.[116] Absorber techniques can be calibrated more accurately than most detection techniques and are used as standards for humidity measurements.[35] Disadvantages include the need for an absorber material that would have to be either replaced or regenerated. This introduces significant complexity and waste generation issues. Additional disadvantages include those common to all techniques in this section.

5. Ex Situ water analysis after solid-liquid extraction

In this category of water analysis, liquid extraction is used to strip water from solid matrices such as impure plutonium materials. The solvent extraction is an alternative to heating to remove the water for *ex situ* analysis. Generic advantages include the lack of need for gas handling systems, the collection of the removed water in a more concentrated form, and the

capability to conduct several stages of analysis on the extractant if necessary. However, the need for solvents, with associated handling and disposal issues, adds complication compared to simple heating. Solvent regeneration and waste handling must also be considered. The degree to which these are significant issues depends on the solvent.

We first discuss water extraction methods and then the associated methods used to quantify water in the extractant. Because many of the quantitative methods are the same as those described above for gas phase water detection, we focus on the unique aspects of the post-extraction application.

5.1 Extraction Methods

Several non-aqueous extractants have been used to separate water from solid hosts that are insoluble in the extractants.[18] The most commonly used extractants are low molecular weight alcohols, in which water has a high solubility. However, water that is bound by strong chemical bonding may not be extracted with high efficiency. Specifically, water molecules in inorganic hydrates may resist extraction by solvents under mild temperatures and pressures. A disadvantage of some otherwise attractive extractants is that they may be hazardous and difficult to treat or recycle. Supercritical carbon dioxide presents a notable exception as discussed below.

Several techniques can be used to detect water once it has been extracted. Karl Fischer titration, in widespread use for many decades, is the most frequently cited method in the recent literature and is generally considered a primary benchmark technique for water determination (see Section 5.2). Other techniques have already been described in preceding sections for gas-phase or solid-phase analysis. Accordingly, in the following discussion we focus only on issues specific to extraction methods. In general, instrumental techniques used to detect water in liquid extractants tend to be less subject to matrix interferences and calibration problems than in solids applications, but more subject to interferences than in gas phase applications. An advantage of extraction methods is that the water is analyzed in a concentrated form that can be transported easily to an instrument that is not in-line in the separation process.

Supercritical carbon dioxide extraction is being investigated actively in the DNFSB 94-1 R/D program for extracting water from impure plutonium materials.[17] In addition to its excellent extracting power for water, supercritical carbon dioxide is environmentally benign and relatively easy to collect and dry for reuse. Results to date indicate that under conditions of elevated temperatures (140 C) and pressures (3000 psi), complete and efficient water extraction (including strongly bound hydrate water) is readily accomplished. Quantitative determination using a hygrometer following vaporization and direct infrared absorption of the supercritical fluid has been demonstrated. These extraction/measurement combinations appear to be inexpensive and practical to install and operate in plutonium processing environments. It shares the disadvantage of many other techniques of requiring sub-sampling of heterogeneous materials.

Our search of Chemical Abstracts through on-line databases found no references to the application of supercritical carbon dioxide extraction to water content determination. Therefore, it cannot be regarded as part of a validated moisture determination method at this time, although it is one with significant promise. The technique is being validated within the DNFSB 94-1 R/D program, and will be considered in a recommendation report expected in Feb. 1999.[13]

5.2 Karl Fischer Titration

Karl Fischer (KF) titration is the most widely accepted standard technique for determining water in a variety of hosts. Many papers on the development of new techniques use Karl Fischer titrations as a standard. The fact that significant numbers of papers continue to be published on this technique (14 Analytical Chemistry articles in 1996-1997) suggests that it remains a premier water analysis method.[117-131] In the KF method, samples first are dissolved or dispersed in an extracting solvent. In the case of insoluble solids, the solvent must be capable of extracting the water from the solid in a reasonable time. The solution is then titrated with Karl Fischer reagent, which is a mixture of iodine, sulfur dioxide, pyridine, and methanol or glycol ether. The titration endpoint is indicated by the appearance of free iodine, which is detected spectrophotometrically or electrochemically.

A recent comprehensive discussion of the KF technique is the monograph of Scholz.[132] In addition to treating the titration itself, this monograph discusses methods for extracting water from solids into a suitable solution for titration. The two most applicable methods to plutonium solids appear to be solvent extraction by methanol, and heating in a flowing gas that is subsequently captured in a solution that can be titrated directly with KF reagent. Notably, KF titrations have been used to determine water on PuO₂ using methanol to extract the water.[123, 125] A group at Argonne National Laboratory is investigating its use to determine moisture in electro-refining salt mixtures.[133]

For routine repetitive application in a plutonium environment, the KF method has the significant disadvantage of being a wet chemical process involving grab sampling, several steps in the analysis, mixing and disposition of reagents, and appreciable operator expertise. Significant recent effort has been devoted to automating the titrations, reducing the volumes of reagents used, and using reagents that are more benign.

5.3 Infrared Spectroscopy

The application of IR methods to water extraction methods is essentially the same as the gas phase IR applications previously described. In the supercritical carbon dioxide method, gaseous water in the carbon dioxide extractant is measured in a high-pressure cell while the carbon dioxide remains in its supercritical fluid state. Supercritical CO₂ as an extractant has advantages over organic extractants, one of which is a simpler infrared spectrum that produces less interference with the water absorption.

5.4 Nuclear Magnetic Resonance

Detection of trace water in extracting solvents by NMR is considerably easier, more specific, more sensitive, and more accurate than the *in situ* detection of water by NMR discussed above. However, high instrumentation and operational costs offset sensitivity or specificity advantages for liquid phase water analysis in a plutonium-processing environment.

5.5 Gas Chromatography

Gas chromatography (GC) has been used to quantify water extracted into both gasses and solutions. This application has a complicated and extensive history which Mitchell and Smith discuss at length in their monograph.[18] Like NMR, GC discriminates water from hydrocarbons and other low-boiling volatile substances. GC instrumentation is inexpensive and adaptable to plutonium operating environments. Sub-sampling would be required, and other disadvantages of using an extraction method are the same as those detailed in the introduction to this section.

5.6 Metal Ion Complexation

Some transition metal ions undergo dramatic color changes in non-aqueous solution when exposed to water due to metal ion complexation and consequent absorption spectrum shifts. A number of sensors based on the water-induced color change of cobalt chloride have been developed. Cobalt chloride is also the indicator whose color changes in the commercial desiccant Drierite™ when it is loaded to capacity with water. Metal ion hydration methods are probably not good candidates for plutonium materials applications because they are wet chemistry procedures requiring dry, non-aqueous solvents. This raises waste and implementation issues. In addition, strongly-bound water may not necessarily be detected due to the limitations of the extractants discussed above.

6. Conclusions

This review considered more than twenty moisture analysis methods and identified a number of techniques that might be applicable to measuring water content of impure plutonium solids. Those classed as *in situ* techniques have the potential to be rapid and to involve minimal (or no) sample preparation. However, in most cases substantial calibration issues complicate actual *in situ* application. Neutron moderation appears to be an almost ideal *in situ* method, if interferences from strong neutron absorbers can be addressed. Results of ongoing validation tests will be presented in a future report.[13]

Of the techniques surveyed which involve preprocessing to separate water from the host matrix prior to water quantitative determination, those that analyze water in the gas phase are most attractive for a number of practical reasons. The most promising gas phase analysis techniques utilize infrared spectroscopy and solid state moisture sensors, both of which are very practical to implement in a plutonium processing environment. Infrared methods are very mature but additional technical assessment of solid state sensors is recommended for plutonium applications.

In general, methods based on liquid extraction of water prior to measurement would be more complicated to implement than thermal methods in glove boxes because organic extractants usually involved. Supercritical carbon dioxide extraction presents a notable exception because the solvent is non-hazardous and reusable. However, this technique is an emergent one that needs additional validation against a widely accepted method such as Karl Fischer titration.

Table I: Summary of how each of the analytical techniques described in this report meet the criteria for application to impure plutonium materials outlined in the overview section. Key to abbreviations: H = high, M = medium, L = low. Sensitivity is categorized as unknown in cases where the literature reviewed for this report does not address sensitivity or discusses it for matrices that cannot easily be related to this application.

| Technique | Specificity for water | Sensitivity | Problematic implementation requirements | | | Cost | Analysis rate | Maturity | Recommendation |
|-----------------------------------|--------------------------|-----------------------|---|------------------|------------|------|------------------|----------|------------------------------------|
| | | | Calibration | Sub- sampling | Deployment | | | | |
| | | | | | | | | | |
| | Analyte | host matrix | | | | | | | |
| Neutron moderation | M | <0.2% | M | L | L | M | H | M | Very promising |
| Microwave | M | <0.2% | H | L | L | L | H | L | Matrix interferences likely |
| IR | M | unknown | H | L | L | L | H | L | Calibration issues prohibitive |
| Proton NMR | M | unknown | H | M | H | H | M | L | Calibration issues prohibitive |
| X-ray diffraction | L | >0.5% | H | M | H | M | M | H | Calibration issues prohibitive |
| | Analyte | processed host matrix | | | | | | | |
| Gravimetric/LOI | L | <0.2% | H | M | L | L | M | H | Calibration issues prohibitive |
| Thermogravimetric | M | <0.2% | M | M | M | L | M | H | Needs enhanced specificity |
| DTA | M | unknown | M | M | M | L | M | H | Needs enhanced specificity |
| Specific heat | M | unknown | H | M | M | M | M | H | Impractical |
| | Analyte | volatilized gas | | | | | | | |
| IR | H | <0.2% | L | M | M | L | M | H | Promising |
| Solid state sensor | H | unknown | M | M | L | L | RT | L | Promising |
| Mass spectrometry | H | <0.2% | M | M | M | M | M | H | Consider for enhanced capabilities |
| Selective absorber | M | unknown | M | M | M | L | M | M | Impractical |
| Mass difference, condensate | M | unknown | L | M | M | L | M | M | Impractical |
| Thermal conductivity of gas | M | unknown | L | M | M | L | M | L | Impractical |
| | Analyte | liquid extractant | | | | | | | |
| IR | H | <0.2% | M | M | M | L | M | H | Additional validation needed |
| Extraction, SC CO2 | H | <0.2% | M | M | M | L | M | M | Additional validation needed |
| Karl Fischer titration | H | <0.2% | L | M | H | M | L | H | Possible reference method |
| Gas chromatography | H | <0.2% | L | M | M | L | M | H | Consider for enhanced capabilities |
| UV/Vis of metal hydrate indicator | H | unknown | M | M | M | L | L | M | Impractical |
| Proton NMR | H | <0.2% | M | M | H | H | M | M | Impractical |

Explanation of column headings:

Specificity for water is the ability to interpret a positive signal as being due to water alone.

Calibration is problematic for diverse sample matrices if the final signal is matrix-dependent. This includes extraction efficiency where relevant.

Sub-sampling is problematic for heterogeneous samples if the technique uses a small sample size.

Deployment can be problematic for diverse reasons, including instrument size, maintenance req., operator training, hazards, waste generation, etc.

Cost is self-explanatory.

Analysis rate includes inherent instrument analysis time and sampling extraction and transportation time.

Maturity summarizes the state of development for this application. Very mature techniques for other moisture analysis applications may be immature for this application.

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